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Journal Name

ARTICLE

Copper Ferrite Nanoparticles Modified Starch as a Highly Recoverable Catalyst for Room Temperature Click Chemistry: Multicomponent Synthesis of 1,2,3-Triazoles in Water

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A new magnetic catalyst comprising starch supported $CuFe_2O_4$ NPs as highly water dispersible material is prepared and characterized by different techniques such as TEM, SEM, VSM, EDX-mapping, XPS, and TG analyses. The obtained $CuFe_2O_4$@Starch is applied as heterogeneous catalyst in click chemistry for the three component synthesis of 1,2,3-triazoles in water at room temperature with low copper loading (0.1 mol%). Using this catalyst, benzylic halides, alkyl bromides and arylboronic acids reacted with sodium azide and terminal alkynes giving 1,4-disubstituted 1,2,3-triazoles in high yields. The catalyst can be easily separated from the reaction mixture using an external magnet and reused for at least 11 consecutive runs with a slight drop in its catalytic activity. The reused catalyst was characterized by TEM, VSM and XPS analysis showing similar structure to fresh catalyst with a slight decrease of the magnetization value and small aggrigations of nanoparticles.

Introduction

In the past two decades sustainable chemistry concerns encourage chemists for design and applications of ecofriendly and biodegradable compounds and catalysts in organic reactions. Among the different biodegradable compounds, starch is one of the completely biodegradable and cheap carbohydrates, which is constructed from large number of glucose units linked by glycosidic bonds. Starch is renewable and can be regenerated from carbon dioxide and water by photosynthesis in plants. Potatoes, wheat and rice contained this material in large amounts.[1] Using heterogeneous catalysts with recoverable and reusable properties is also in line with the objectives of sustainable chemistry standpoints.[2] However, less efficiency of heterogeneous catalysts with compared to their homogeneous counterparts and separation problems of these catalysts by simple filtration or centrifugation methods are two important drawbacks of heterogeneous catalysis. One of the best solutions to overcome these problems is the use of magnetic catalysts having large ratio of surface area to volume, low toxicity and superparamagnetic behavior. These type of magnetic supports allow the simple separation from the reaction mixture by an external magnetic field.[2] In order to improve the properties of magnetic nanoparticles derived catalysts, increasing attention have been recently paid to modify magnetic nanoparticles with different compounds and ligands.[3]

Among the different magnetic compounds, $CuFe_2O_4$ NPs with a spinel structure have received great attention because of several advantages such as environmental compatibility, moisture insensitive, high dispersion and reactivity, low cost, and easy separation by an external magnet. Due to synergetic catalytic effect between copper and iron atoms, recently, $CuFe_2O_4$ NPs have attracted great attention as a magnetically recoverable catalyst in different organic transformations.[4] Along this line, we have reported $CuFe_2O_4$ as magnetic catalysts in C-S bond formation for the synthesis of thioethers and trithiocarbonates[5] and $CuFe_2O_4$/PdNPs@SiO_2 acted as a recoverable catalyst in cyanation reactions of aryl halides with $K_4[Fe(CN)_6]$.[6] In the case of Sonogashira reaction $CuFe_2O_4$/PdNPs@SiO_2[7a] and $CuFe_2O_4$/Au@SiO_2[7b] enhanced the catalytic efficiency in this reaction.

The copper-catalyzed cycloaddition reaction of terminal alkynes with organic azides (CuAAC) is one of the most attractive synthetic tools for formation of highly regioselective 1,4-disubstituted 1,2,3-triazole derivatives.[8] Nitrogen heterocyclic compounds obtained from the click reaction have different industrial applications for the preparation of dyes,

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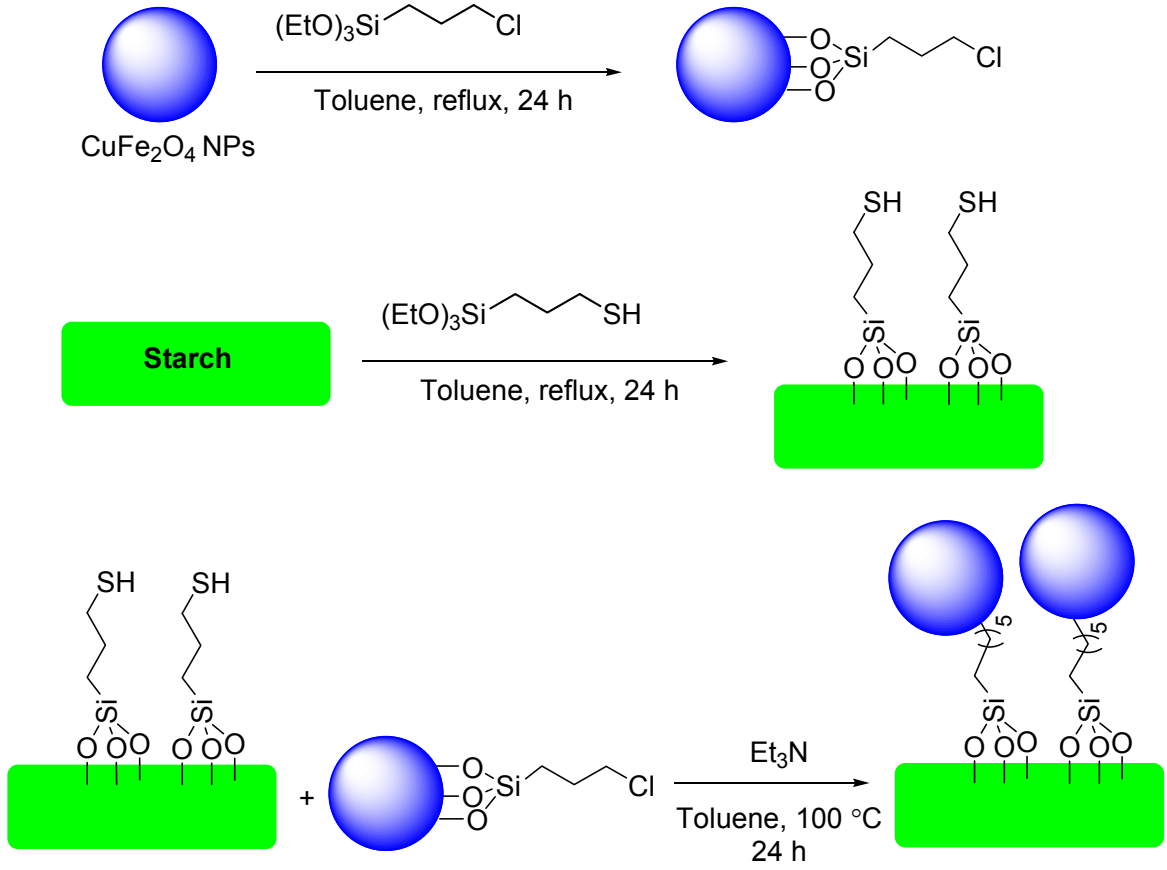
drugs, corrosion inhibitors (of copper and copper alloys), photostabilizers, photographic materials, and agrochemicals.[9] In recent years, different heterogeneous and homogeneous copper catalysts have been applied for click reaction.[10-11] However, to date few magnetic copper catalysts have been prepared and successfully applied for azide–alkyne cycloaddition reaction.[12] Recent applications of $CuFe_2O_4$ NPs for the click reaction were performed using different alkyl azides and alkynes.[13-14] These reactions proceed using water as solvent at 70 °C[13] or by addition of 2,2-bipyridine as ligand and Et_3N as base.[14] It should be noted that dispersibility of $CuFe_2O_4$ in aqueous media is very low and attaching hydrophilic compounds and ligands to the $CuFe_2O_4$ NPS surface provides superior dispersion of particles and increase reactivity of the catalyst in aqueous media. For this purpose, in this work we introduce highly water dispersible starch modified $CuFe_2O_4$ NPs as a very efficient and sustainable magnetically recyclable catalyst for click chemistry in the multicomponent synthesis of 1,2,3-triazole derivatives in neat water at room temperature.

Results and discussion

For the preparation of $CuFe_2O_4$ modified starch, the corresponding $CuFe_2O_4$ NPs were synthesized through the conventional co-precipitation method using $FeCl_3$ and $CuCl_2.2H_2O$ in an argon atmosphere.[4d] The synthesized $CuFe_2O_4$ NPs were allowed to react with 3-chloropropyltriethoxysilane in dry toluene giving Cl@$CuFe_2O_4$. Starch containing the thiol functional group, SH@Starch, was prepared by reaction of starch with 3-mercaptopropyl triethoxysilane in dry toluene. The grafting of $CuFe_2O_4$ to starch was achieved by mixing SH@Starch and Cl@$CuFe_2O_4$ in toluene at reflux for 24 h affording the expected $CuFe_2O_4$@Starch (Scheme 1).



Scheme 1. Preparation of $CuFe_2O_4$@Starch

A transmission electron microscopy (TEM) image of the prepared $CuFe_2O_4$ NPs confirmed the formation of nanoparticles of average size 20 nm (Fig. 1). Furthermore, TEM images of final $CuFe_2O_4$@Starch showed presence of $CuFe_2O_4$ NPs attached to starch network (Fig. 2).

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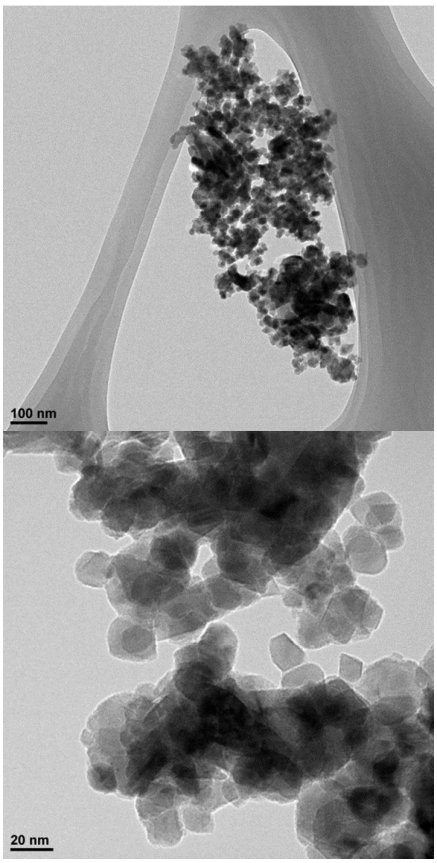
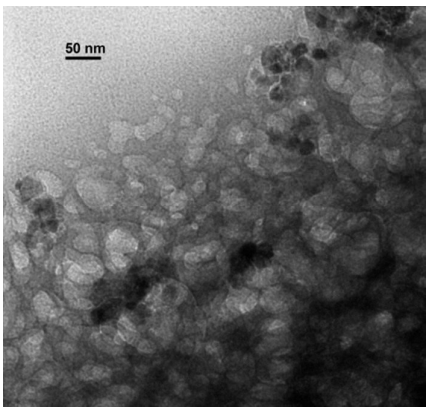


Fig. 1 TEM images of prepared $CuFe_2O_4$ NPs



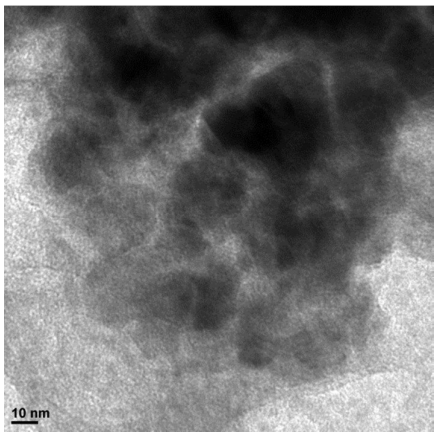


Fig. 2 TEM images of prepared $CuFe_2O_4$@Starch

Particle size distribution plots obtained from TEM measurements for $CuFe_2O_4$ and $CuFe_2O_4$@Starch confirmed major parts of the particles are located between 10-30 nanometers (Fig. 3).

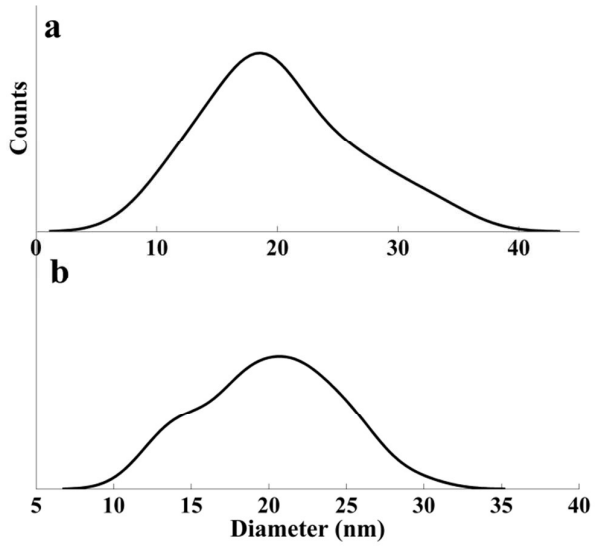


Fig. 3 Particle size distribution plot obtained from TEM measurement for a) CuFe2O4 NPs and b) CuFe2O4@Starch

The corresponding SEM image of $CuFe_2O_4$@Starch showed the presence of uniform particles in micrometer size, which are related to starch particles. Furthermore, EDS mapping images of the $CuFe_2O_4$@Starch indicated the presence of uniformly dispersed Fe, C and Cu in the structure (Fig. 4).

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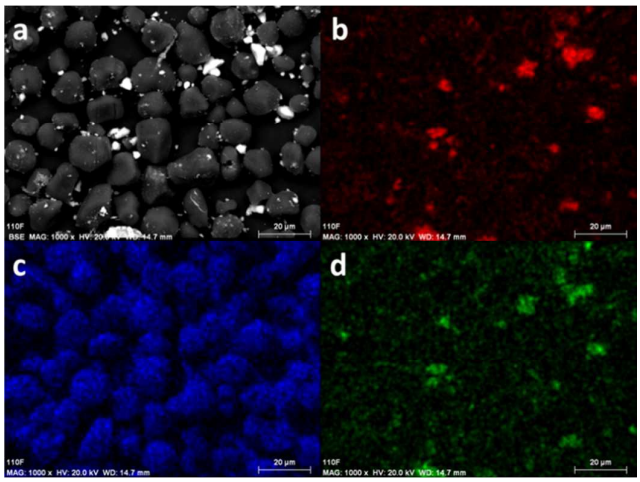

Fig. 4 SEM image (a) and EDS mapping images of Fe (b), C (c) and Cu(d).

The magnetic properties of the prepared samples have been analyzed by Vibrating Sample Magnetometer (VSM). Results showed zero coercivity and remanence on the magnetization loop without the presence of a hysteresis loop, which is characteristic for superparamagnetic materials.[15] Decrease in the magnetization value of the $CuFe_2O_4$@Starch (4.3 $emug^{-1}$) in comparison with $CuFe_2O_4$ (29.5 $emug^{-1}$) confirms the successful attachment of $CuFe_2O_4$ on starch polysaccharide network (Fig. 5).

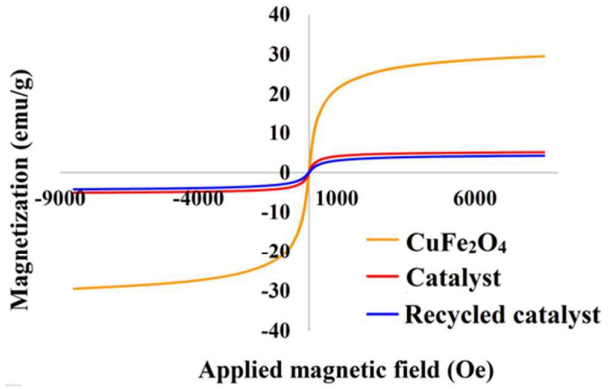

Fig. 5 Magnetization curves of $CuFe_2O_4$, $CuFe_2O_4$@Starch (catalyst) and of the recycled catalyst after the 12th run.

Further insight into the surface composition of the $CuFe_2O_4$@Starch was obtained from X-ray photoelectron spectroscopy (XPS) (Fig. 6). For the XPS of Cu 2p regions, the binding energy for Cu 2p3/2 is located at 932.9 eV with a shake-up satellite at 943.6 eV, and for Cu 2p1/2 is observed at 952.7 eV with a satellite at 962.7 eV. The main peaks at binding energies of 932.9 eV and 952.7eV (Cu2p3/2 and Cu2p1/2) are assigned to Cu^{2+} on octahedral sites, while the minor ones at 954.5 eV and 934.9eV can be assigned to Cu^{2+} on tetrahedral coordination sites (Fig. 6a).[16] Also, the high resolution narrow scan for Fe2p showed two peaks centered at 710.4 eV and 724.1eV corresponds to Fe 2p3/2 and Fe 2p1/2 and are due to Fe(II) species. The peaks centered on 712.5 and 725.1 eV, corresponding to Fe 2p3/2 and Fe 2p1/2, respectively, and are consistent with typical values for the ferric oxides. The peak at 718.5 eV is a satellite peak for the above four peaks, indicating the co-existence of Fe(III) and Fe(II) in the catalyst (Figure 6b).[1] XPS analysis further confirmed the presence of carbon of starch by showing a peak related to C1s at 184.6, 286.3 and 288.4 eV related to C-C/C-H, C-O and O-C-O respectively (Fig. 6c).[17]

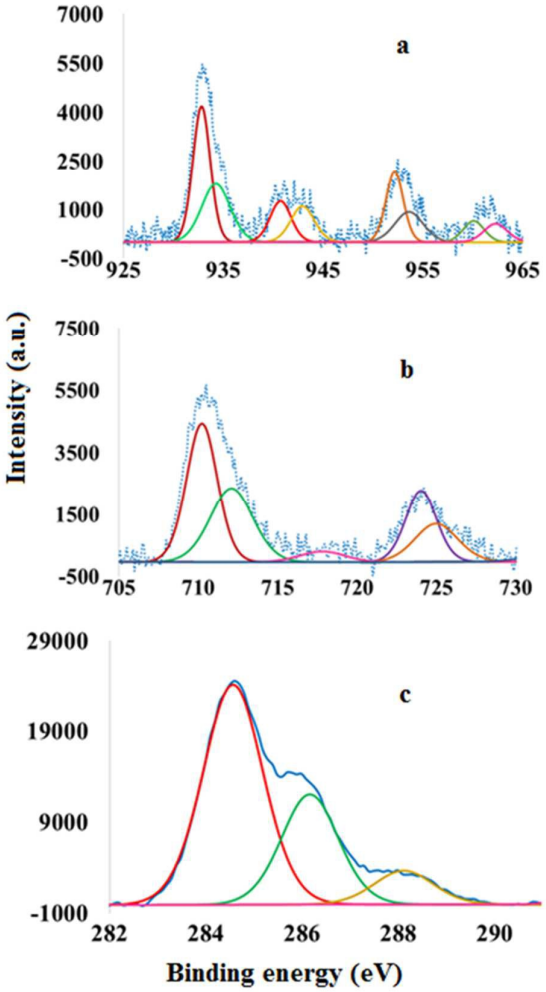

Fig. 6 XPS spectrum of $CuFe_2O_4$@Starch in a) Cu 2p, b) Fe 2p and c) C 1s regions

Thermogravimetric analysis (TGA) of prepared $CuFe_2O_4$@Starch showed two main weight losses between 25 and 800 °C. First weight loss (50–150) is related to physically adsorbed water and organic solvents and second one is related to decomposition of starch polysaccharide structure. This diagram confirms thermal stability and negligible structure leaching of $CuFe_2O_4$@Starch up to 280 °C (Fig. 7).

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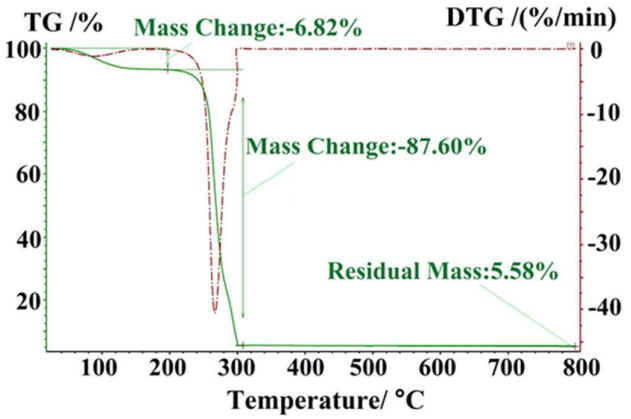
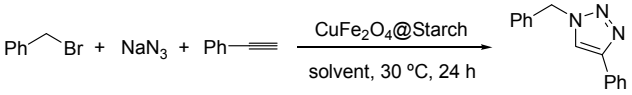


Fig. 7 Thermogravimetric diagram of $CuFe_2O_4$@Starch

We have tested the catalytic activity of the prepared magnetic material in 1,3-dipolar cycloaddition of azides and alkynes. Initially, reaction of benzyl bromide, sodium azide, and phenylacetylene was selected as a model reaction and effects of different reaction conditions such as solvent and amount of catalyst were studied (Table 1). Using 0.1 mol% of catalyst in different solvents such as CH_3CN, EtOH, THF, DMF, and toluene afforded low yields for the reaction at room temperature (Table 1, entries 1-5). Among the solvents tested, H_2O was the most suitable reaction media for the reaction (Table 1, entry 6). Using H_2O as solvent, the reaction was carried out with 0.06 and 0.04 mol% loadings affording the corresponding triazole in 73 and 64% yield, respectively (Table 1, entries 7-8).

Table 1. Optimization of the reaction conditions for the reaction of benzyl bromide, sodium azide, and phenylacetylene

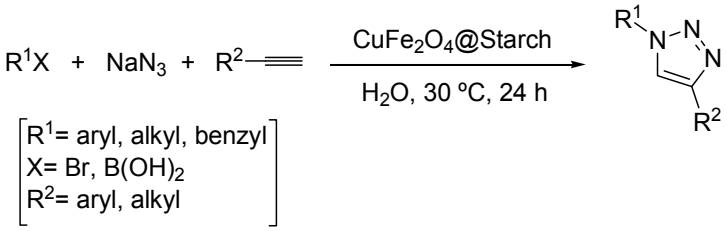


Entry	Catalyst (mol %)	Solvent	Yield (%)
1	0.1	CH_3CN	7
2	0.1	EtOH	32
3	0.1	THF	39
4	0.1	DMF	17
5	0.1	Toluene	5
6	0.1	H_2O	92
7	0.06	H_2O	73
8	0.04	H_2O	64

[a]Reaction condition: benzyl bromide (1 mmol), NaN_3 (1.5 mmol), phenylacetylene (1.5 mmol), and solvent (2 mL)

Having the optimized reaction conditions in hand, the scope of this reaction with different alkyl halides and acetylenes was studied. Reactions of benzyl halides with sodium azide and phenylacetylene afforded the corresponding triazoles in high to excellent yields (Table 2, entries 1-5). Also, reactions of *ortho* substituted benzyl bromides were performed efficiently and gave corresponding products in 76-85% isolated yields (Table 2, entries 6-7). Reactions of benzyl bromides with other alkynes such as 4-ethynyltoluene, 4-ethynylanisole and propargyl alcohol took place efficiently (Table 2, entries 8-11). Furthermore, reaction of 2-bromoethyl benzene as well as other aliphatic alkyl bromides proceeded efficiently and gave corresponding products in 78-91% isolated yields (Table 2, entries 12-15). When arylboronic acids were allowed to react with sodium azide and phenylacetylene, under the optimized reaction conditions, the corresponding 1,2,3-triazole derivatives were obtained in 80-83% isolated yields (Table 2, entries 16-19).

Table 2. Multicomponent Synthesis of Triazoles at Room Temperature Using Water as Solvent and $CuFe_2O_4$@Starch as Catalyst.



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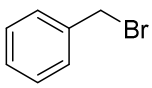
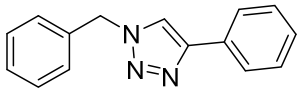
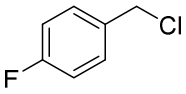
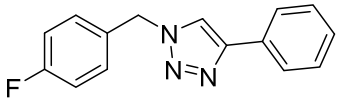
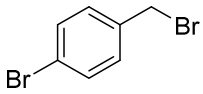
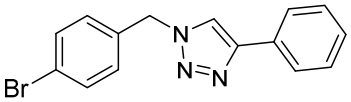
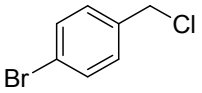
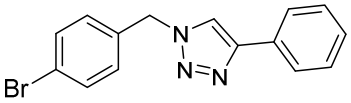
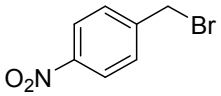
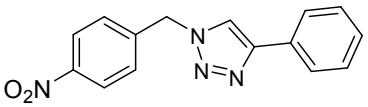
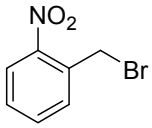
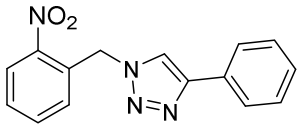
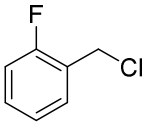
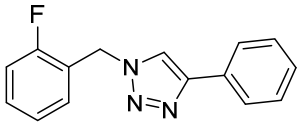
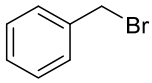
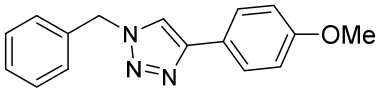
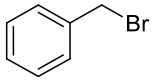
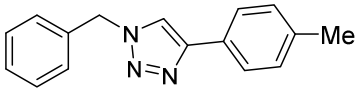
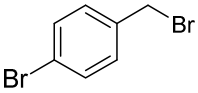
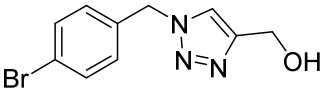
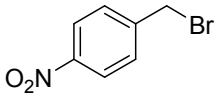
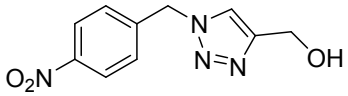
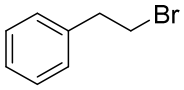
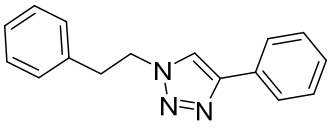
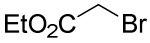
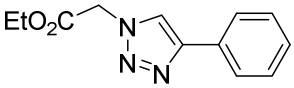
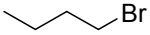
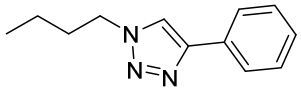
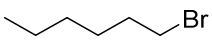
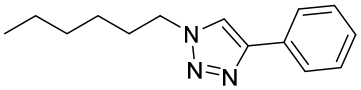
Entry	RX	R^2	Product	Isolated yields
1		Ph		92
2		Ph		84
3		Ph		89
4		Ph		83
5		Ph		90
6		Ph		85
7		Ph		76
8		4-OMe C_6H_4		95
9		4-Me C_6H_4		93
10		CH_2OH		82
11		CH_2OH		85
12		Ph		87
13		Ph		91
14		Ph		82
15		Ph		78

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16	Ph	82
17	Ph	80
18	4-Me C_6H_4	82
19	4-OMe C_6H_4	83

[a]Reaction condition: R^1X (1 mmol), NaN_3 (1.5 mmol), alkyne (1.5 mmol), and H_2O (2 mL) and catalyst

We have also studied large-scale laboratory application for the reaction of benzyl bromide (10 mmol), sodium azide (15mmol) and phenylacetylene (15 mmol) under optimized reaction conditions. Result showed reaction proceed well and afford 90% isolated yield for the desired product.

Finally the recyclable ability of the catalyst has been studied for the benchmark reaction of benzyl bromide, sodium azide, and phenylacetylene. After completion of the reaction, the resulting suspension was subjected to external magnet and after washing and drying the separated catalyst was used for another reaction batch. Results showed that yield of reaction was decreased from 92% to 90% in run 5 and from run 5 to 11, the yield decreased to 84%. However, in run 12, the yield of the reaction was significantly decreased to 68%. These results indicated that the catalyst is recyclable for 11 runs with small decrease in activity (Fig 8).

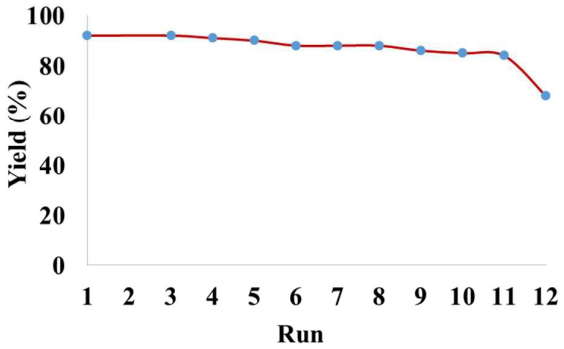
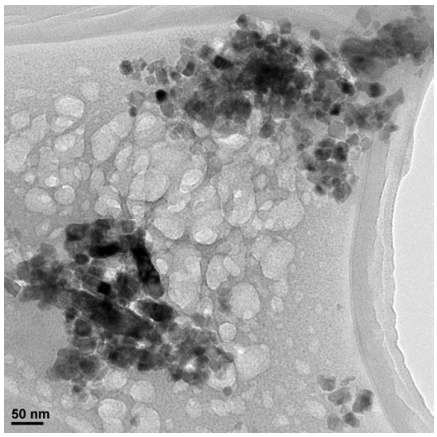


Fig. 8 Recycling of the catalyst for the reaction of benzyl bromide, sodium azide and phenylacetylene.

TEM images of the catalyst after 12 runs showed the preserve of catalyst structure with small aggregation of nanoparticles (Fig. 9). Also, XPS analysis of reused catalyst after 12 runs showed preserve of structure by showing related peaks to Cu 2p, F2p and C1s elements (Fig. 10). Superparamagnetic properties of the recycled catalyst after the 12 run showed a very slight decrease in the magnetization value (Fig. 5).



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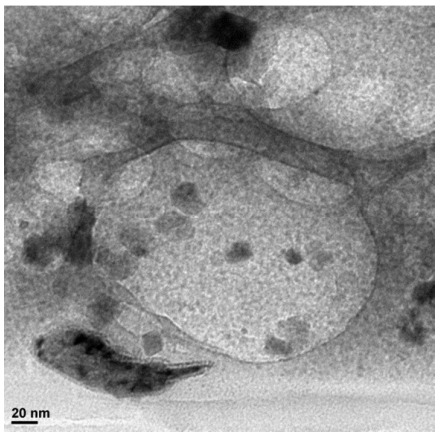

Fig. 9 TEM images of reused catalyst after 12 runs.

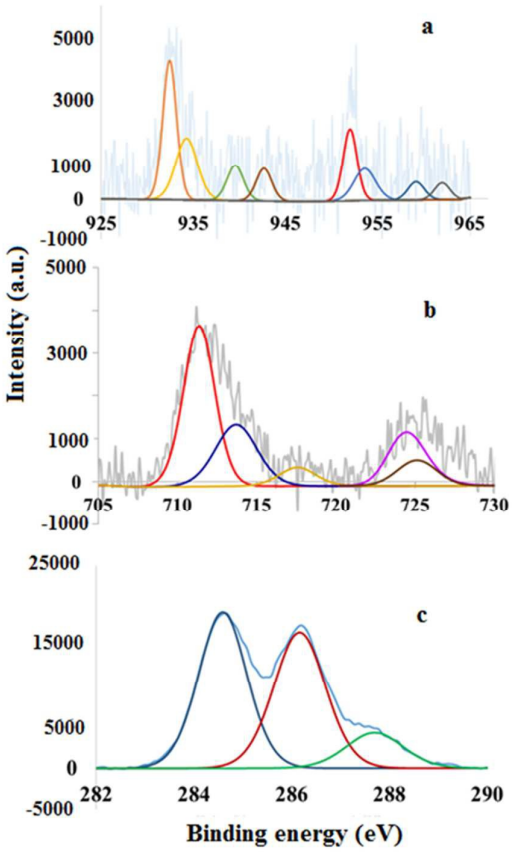

Fig. 10 XPS spectrum of the reused catalyst after 12 runs in a) Cu 2p, b) Fe 2p and c) C 1s regions

Conclusions

In conclusion, in this work we have prepared $CuFe_2O_4$@Starch a highly water dispersible, efficient and magnetically separable heterogeneous catalyst for click synthesis of 1,2,3-triazoles in water. Using this catalyst, various alkyl halides as well as arylboronic acids reacted efficiently with sodium azide and alkynes. This catalyst was recycled up to eleven times with small decrease in its activity and the fresh and recovered catalysts were adequately characterized by spectroscopic and microscopic techniques.

Experimental

Synthesis of (3-mercaptopropyl)triethoxysilane functionalized starch (SH@Starch)

Starch (1 g) was dispersed by sonication during 15 min in dry toluene (15 mL). To the resulting suspension, (3-mercaptopropyl)triethoxysilane (3 mmol, 0.72 mL) was added and the mixture was stirred under reflux for 24 h under argon atmosphere. Then, the reaction mixture was subjected to centrifugation and 3-mercaptopropyl triethoxysilane functionalized starch (SH@Starch) was separated. The solid was washed successively with EtOH (20 mL) and CH_2Cl_2 (10 mL) and dried under vacuum for 24 h.

Synthesis of (3-chloropropyl)triethoxysilane functionalized $CuFe_2O_4$ nanoparticles Cl@$CuFe_2O_4$

$CuFe_2O_4$ nanoparticles were synthesized by the procedures described previously.[4d] $CuFe_2O_4$ NPs (500 mg) were dispersed in dry toluene (15 mL) for 30 min using ultrasound assistance. To the resulting suspension, (3-chloropropyl) triethoxysilane (2 mmol, 0.48 mL) was added and the mixture was refluxed for 24 h under argon atmosphere. The (3-chloropropyl) triethoxysilane functionalized $CuFe_2O_4$ NPs (Cl@$CuFe_2O_4$) was subjected to magnetic separation, and was washed sequentially with EtOH (3× 20 mL) and dried under vacuum.

Grafting of Cl@$CuFe_2O_4$NPs on SH@Starch:

Cl@$CuFe_2O_4$NPs (100 mg) and SH@Starch (600 mg) were dispersed separately in toluene (15 mL) for 30 min and then mixed together. To the resulting mixture, Et_3N (2 mmol, 0.28 mL) was added and reaction mixture refluxed for 24 h under argon atmosphere. Then, the mixture was subjected to magnetic separation and the isolated $CuFe_2O_4$@Starch were washed sequentially with CH_2Cl_2 (2× 10 mL) and dried under vacuum for 24 h.

General procedure for Synthesis of 1,2,3-Triazoles using $CuFe_2O_4$@Starch

To a flask containing catalyst (0.1 mol%, 15 mg) were added benzyl halide, alkyl halide or arylboronic acid (1 mmol), sodium azide (1.5 mmol, 97.5 mg), alkyne (1.5 mmol), and H_2O (2 mL). The mixture was stirred at room temperature for 24 h under air atmosphere. Then, mixture was washed with ethyl acetate (3×15 mL) to extract crude products. Further purification of products was achieved with column or plate chromatography using hexane and ethyl acetate as eluents.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Table of Content Entry:

Highly water dispersible $CuFe_2O_4$@Starch catalyzed click reaction